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## Effect of Ba and Bi doping on the synthesis and sintering of Ge-based apatite phases

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**Abstract** Recently, high oxide ion conduction has been observed in the apatite-type systems  $\text{La}_{9.33+x}(\text{Si}/\text{Ge})_6\text{O}_{26+x/2}$ , with conductivities approaching and even exceeding that of yttria-stabilized zirconia. The Ge-based phases have been reported to suffer from Ge loss and undergo irreversible structural changes on sintering at the high temperatures required to obtain dense pellets. In this paper we discuss doping studies (Ba, Bi for La) aimed at stabilizing the hexagonal apatite lattice to high temperature, and/or lowering the synthesis and sintering temperatures. The results show that doping with Ba helps to stabilize the hexagonal lattice at high temperatures, although Ge loss appears to still be a problem. Conductivity data show that, as previously reported for the Si-based systems, non-stoichiometry in the form of cation vacancies and/or oxygen excess is required to achieve high oxide ion conduction in these Ge-based systems. Neutron diffraction structural data for the fully stoichiometric phase  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  shows that the channel oxygen atoms show little anisotropy in their thermal displacement parameters, consistent with the low oxide ion conductivity of this phase. Bi doping is shown to lower the synthesis and sintering temperatures, although the presence of Bi means that these samples are not stable at high temperatures under reducing conditions.

**Keywords** Apatite · Germanium · Oxide ion conduction · Solid oxide fuel cells

### Introduction

Oxide ion conducting materials are attracting considerable interest due to a range of technological uses, e.g. as oxygen sensors, oxygen separation membranes or electrolytes for solid oxide fuel cells (SOFCs). There is huge amount of literature on materials with perovskite or fluorite-type structures, but results for other structure types are less widespread. In terms of the latter, apatite-type materials,  $\text{La}_{10-x}(\text{Si}/\text{Ge})_6\text{O}_{26+y}$ , have begun to attract significant interest. This work has been driven by the initial reports from Nakayama et al. [1, 2, 3] showing high oxide ion conductivity in the system  $\text{La}_{10-x}\text{Si}_6\text{O}_{26+y}$ . Since these initial results, a range of doping studies has been performed to try to optimize the oxide ion conductivities of these interesting materials [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. Most of the studies have focused on Si-based apatite materials, since high-quality samples are more readily obtained in such cases. The results from these studies have shown that non-stoichiometry in the form of either cation vacancies or oxygen excess is required to achieve high oxide ion conduction. Structural and computer modelling studies have attributed this to the presence of interstitial oxide ions in such systems [5, 14, 15, 16]. There is therefore a growing understanding of the process of oxide ion conduction and its optimization in the Si-based systems.

In contrast, research on the corresponding Ge-based systems  $\text{La}_{10-x}\text{Ge}_6\text{O}_{26+y}$  has suffered from conflicting reports, and controversy regarding the exact nature of the conducting phase. Consequently, very little is known about the nature of the oxide ion conduction in these particular systems. The Ge-based materials  $\text{La}_{10-x}\text{Ge}_6\text{O}_{26+y}$  were initially reported by Arikawa et al. [7] as apatite-type. Subsequently, the same group reported that the conducting phase was not apatite-type but rather cation-deficient  $\text{La}_{2-x}\text{GeO}_{5-3x/2}$  [8]. More recent work in our group [10] and by Berastegui et al. [13] has concluded that the conducting phase is indeed apatite-type. The confusion arises from irreversible changes that

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occur on sintering samples at the high temperatures required to achieve dense pellets for conductivity measurements. Results have shown that  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ , with the hexagonal apatite lattice, can be prepared at intermediate temperatures ( $\sim 1150$  °C). Heating this phase to higher temperatures (typically around 1300–1350 °C) results firstly in peak broadening in the X-ray diffraction pattern, which has been attributed to a correlated disorder within the apatite channels by Berastegui et al. [13]. Further heating to even higher temperatures ( $> 1350$  °C), required for sintering pellets, results in the occurrence of distinct extra peaks either side of the main apatite peaks. The X-ray pattern, however, still resembles that of an apatite-type phase (possibly triclinic) rather than  $\text{La}_2\text{GeO}_5$  [10, 13]. Further support for the conclusion that the conducting phase is apatite-type rather than  $\text{La}_2\text{GeO}_5$ -type was provided by Berastegui et al. [13]. The authors tried to incorporate La cation vacancies into  $\text{La}_2\text{GeO}_5$  and observed significant impurities as well as no change in the unit cell for the  $\text{La}_2\text{GeO}_5$ , suggesting that the  $\text{La}_2\text{GeO}_5$  structure will incorporate negligible cation vacancies. Our own unpublished data on the  $\text{La}_2\text{GeO}_5$  system is in complete agreement with the conclusions of Berastegui et al.

The origin of the irreversible changes in the X-ray patterns on heating  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  to high temperatures appears to be related to Ge volatility [10, 13]. Evidence for this was provided by our previous work [10], in which we examined the effect of an extended sintering treatment (1500 °C for 5 days) of a sample of  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ . This was shown to result in significant mass loss, with the X-ray pattern changing to that of  $\text{La}_2\text{GeO}_5$ , while the conductivity dropped nearly three orders of magnitude. Since Ge is the most volatile component in the sample, and the system had changed composition to a phase with a lower percentage Ge content, the mass loss was attributed to Ge volatility.

As a result of these problems encountered with undoped  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ , we have been investigating ways of stabilizing the hexagonal apatite lattice in this system to high temperatures, and/or lowering the synthesis/sintering temperatures. To this end we have performed a range of doping studies. In particular, we have examined the effect of doping with alkaline earth elements and other divalent cations onto the La site, and data for Ba doping is reported here. In addition, we have examined the effect of Bi doping onto the La site to lower the synthesis/sintering temperature. In addition to the synthesis and conductivities of the doped phases, we also report some studies of long-term sintering stability to

determine whether Ge loss is still a problem. A structural study of the Ba-doped phase,  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$ , is also reported.

## Experimental

High-purity  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{GeO}_2$  were used to prepare a range of Ba-doped samples. The samples were prepared as follows: the powders were intimately mixed in the correct ratios and heated to 1150 °C for 16 h; the resultant powders were reground and reheated at 1200–1350 °C for a further 16 h.

For the Bi-doped samples a range of samples with other codopants (Ba, Sr, Ga) was prepared. High-purity  $\text{La}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{GeO}_2$  and  $\text{Ga}_2\text{O}_3$  were used, and the intimately mixed powders were first heated at 950–1000 °C for 12 h; the sample was then reground and reheated at 1050–1100 °C for 8 h.

Conductivities were determined from AC impedance measurements (Solartron 1260 Impedance analyser). Pellets (1.6 cm diameter) were pressed under a pressure of 8000 kg/cm<sup>2</sup> and sintered at 1600 °C for 2 h for the La-Ba-Ge-O samples. For the Bi-doped samples the sintering temperature was 1050–1100 °C for 4 h. Pellet densities  $> 85\%$  theoretical were achieved. Owing to general problems, experienced previously with these apatite systems [4, 5, 9, 10], in reliably resolving bulk and grain boundary semicircles, the conductivity data reported represent the total conductivity.

Extended sintering studies were performed for some samples, to determine whether Ge loss problems were still observed in the doped samples. Pellets were heated at 1500 °C for 5 days, after which the conductivity was measured and an X-ray pattern recorded.

Neutron powder diffraction data were collected for the sample  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  on diffractometer POLARIS, ISIS, Rutherford Appleton Laboratory. Structure refinement was performed by the Rietveld method, using the GSAS suite of programs [18].

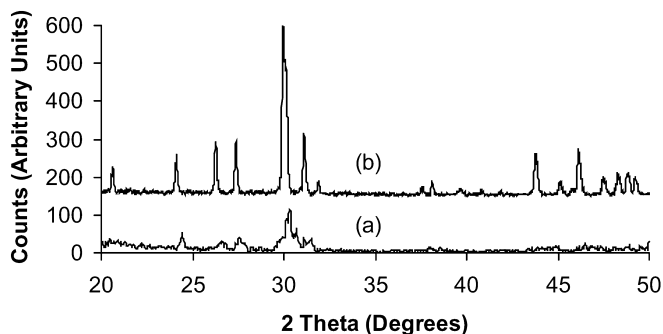
## Results and discussion

### Ba doping

Our preliminary studies have shown that doping a range of divalent cations onto the La site in  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ , i.e.  $\text{La}_{9.33-x}\text{M}_{3x/2}\text{Ge}_6\text{O}_{26}$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Ca}, \text{Sr}, \text{Ba}$ ), is successful in stabilizing the hexagonal apatite lattice at the high temperatures (1600 °C) required for sintering. A wide range of samples has been prepared and the full characterization of these materials is ongoing. In this paper we report data for the Ba-doped samples. Cell parameter and conductivity data for a selection of samples are given in Table 1. The cell parameter data show an increase with increasing Ba content due to the larger size of Ba compared to La, supporting the successful substitution of Ba into the structure. As stated, the Ba doping helps to stabilize

**Table 1** Cell parameter (hexagonal cell) and conductivity data for Ba-doped  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$

| Sample composition                               | $a = b$ (Å) | $c$ (Å)  | $\sigma$ (S cm <sup>-1</sup> ) (800 °C) | $E_a$ (eV) (low/high temperature) |
|--|-------------|----------|---|-----------------------------------|
| $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$       | 9.913(3)    | 7.282(3) | 0.01                                    | 1.28/1.62                         |
| $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$ | 9.983(1)    | 7.405(1) | $5.5 \times 10^{-5}$                    | 1.05/0.62                         |
| $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$        | 9.940(3)    | 7.363(3) | 0.03                                    | 1.13/0.94                         |
| $\text{La}_{8.67}\text{BaGe}_6\text{O}_{26}$     | 9.951(4)    | 7.355(3) | 0.008                                   | 0.97                              |

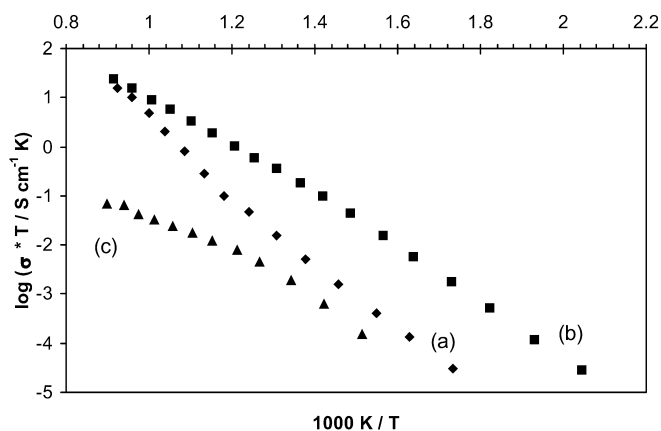


**Fig. 1** X-ray diffraction patterns for sintered (1600 °C, 2 h) pellets of (a)  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  and (b)  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$

the hexagonal apatite lattice to high temperatures, and to emphasize this, the X-ray patterns for the sintered (1600 °C) pellets of  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  and  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  are shown in Fig. 1.

Previous doping studies of corresponding Si-based systems, e.g.  $\text{La}_{9.33-x}\text{Ba}_y\text{Si}_6\text{O}_{26+z}$ , had shown that in order to achieve high oxide ion conduction in these apatite systems, non-stoichiometry in the form of cation vacancies and/or oxygen excess was required, with the highest conductivities being observed for samples containing oxygen excess [5, 11, 16]. Similarly for the Ge-based systems studied here, high conductivities were obtained for samples with cation vacancies or oxygen excess, while the conductivity of  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$ , which is nominally fully stoichiometric (on both cation and anion sites), was low. This can clearly be seen from Table 1 and the conductivity plots for the samples  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ ,  $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$  and  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  (Fig. 2).

Interestingly, although the conductivity of  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  is rather poor, the activation energy for oxide ion conduction in this phase is surprisingly low, particularly in the high-temperature region (Table 1), contrary to that observed for the related Si-based system  $\text{La}_8\text{Ba}_2\text{Si}_6\text{O}_{26}$  ( $E_a = 1.21$  eV) [11]. This suggests that there



**Fig. 2** Conductivity data for (a)  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ , (b)  $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$  and (c)  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$

are some mobile oxygen ions in the sample, although they are few in number, and hence the overall conductivity is low. The origin of these mobile oxygens could be the introduction of a small degree of non-stoichiometry due to partial Ge loss on sintering.

As for the Si-based systems, the sample with oxygen excess,  $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$ , showed the highest conductivity, supporting the importance of interstitial oxide ions also for the Ge-based systems.

#### Structural determination of $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$

Neutron powder diffraction data were collected for  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  to try to account for the low oxide ion conductivity of this sample. Three possible space groups were investigated,  $P-3$ ,  $P6_3$  and  $P6_3/m$ , in accordance with previous studies of apatite-type systems. As with our previous refinements of the structures of  $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$  and  $\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$  [5], the best fit was obtained for space group  $P-3$ , and so this space group was used in the final refinement. Refinement of the La/Ba occupancies suggested that there was negligible Ba on the La1 and La3 sites, with Ba instead favouring occupancy of the La2 site. Therefore, in the final refinement, all the Ba was placed on this site. Table 2 gives the final refined structural parameters, with selected bond distances given in Table 3.

The observed, calculated and difference profiles for both samples are given in Fig. 3. The data indicate that there is negligible occupancy of Ba in the La3 site, which is the La site closest to the oxide ion channels. This preference for lower charge cations (e.g. Sr, Ba)/cation vacancies on the La1/La2 sites (the La sites away from the oxide ion channels) has been previously observed in structural studies of related systems [5, 13, 16]. It is especially interesting that in this particular case there is ordering between the La1 and La2 sites, such that Ba appears to favour occupancy of the La2 site. These two sites are one site in space group  $P6_3/m$ , and so this ordering of Ba could be the origin of the reduction in cell symmetry to space group  $P-3$ . In this respect, the  $R$  factors for refinement with space group  $P-3$  were noticeably lower than for space group  $P6_3/m$  [ $R_{wp} = 2.08\%$  ( $P-3$ ) versus  $2.46\%$  ( $P6_3/m$ )], as stated earlier.

Apart from the ordering of Ba on the La2 site, a further key feature of the refinement is that although the anisotropic thermal displacement parameters of the channel oxygen atoms (O5) are relatively high, the anisotropy in these values (Table 2) is much lower than reported for previous structural studies on highly conducting apatite samples, such as  $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$  [5, 13, 16]. In these latter cases, there was large anisotropy in the thermal displacement parameters for this oxygen, with particularly high values for motion down the channels, consistent with the high oxide ion conduction. In the present case, however, the values for  $U_{11}/U_{22}$  and  $U_{33}$  are much more similar, such that they are closer to being

**Table 2** Structural parameters<sup>a,b</sup> for La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub>

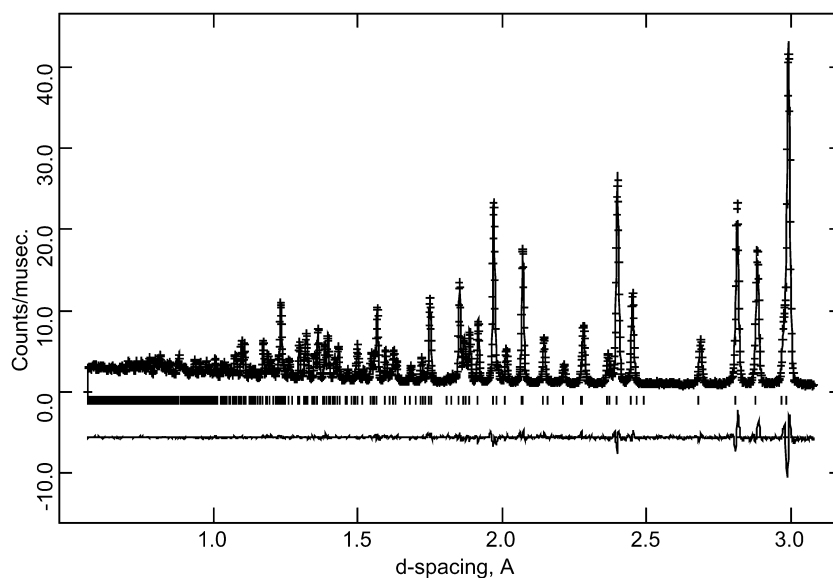
| Atom    | Site   | X         | Y         | Z          | $U_{\text{iso}} (\times 100)$ | SOF     |
|---------|--------|-----------|-----------|------------|-------------------------------|---------|
| La1/Ba1 | 2b     | 1/3       | 2/3       | -0.0018(8) | 0.7(1)                        | 1.0/0.0 |
| La2/Ba2 | 2b     | 2/3       | 1/3       | 0.499(1)   | 0.1(1)                        | 0.0/1.0 |
| La3     | 6c     | 0.0105(2) | 0.2408(1) | 0.2518(7)  | 0.93(2)                       | 1.0000  |
| Ge      | 6c     | 0.3991(1) | 0.3709(1) | 0.2458(5)  | 0.65(2)                       | 1.0000  |
| O1      | 6c     | 0.3152(2) | 0.4861(2) | 0.252(1)   | 1.95*                         | 1.0000  |
| O2      | 6c     | 0.6012(2) | 0.4757(3) | 0.243(1)   | 2.04*                         | 1.0000  |
| O3      | 6c     | 0.3367(8) | 0.2486(7) | 0.0643(6)  | 2.25*                         | 1.0000  |
| O4      | 6c     | 0.3469(7) | 0.2479(8) | 0.4378(6)  | 2.43*                         | 1.0000  |
| O5      | 2a     | 0.0000    | 0.0000    | 0.246(3)   | 3.04*                         | 1.0000  |
|         | U11    | U22       | U33       | U12        | U13                           | U23     |
| O1      | 3.3(1) | 1.9(1)    | 2.3(1)    | 2.3(1)     | 0.0(3)                        | 0.0(3)  |
| O2      | 1.4(1) | 1.0(1)    | 3.4(2)    | 0.22(7)    | 0.7(3)                        | -0.1(3) |
| O3      | 6.6(4) | 1.7(2)    | 0.8(2)    | 2.6(3)     | -3.5(2)                       | -2.0(2) |
| O4      | 3.2(3) | 2.4(3)    | 2.4(2)    | 1.7(2)     | -0.6(2)                       | -0.3(2) |
| O5      | 2.5(1) | 2.5(1)    | 4.0(2)    | 1.26(5)    | -                             | -       |

<sup>a</sup>Space group = *P*-3 (no. 147),  $a = b = 9.9828(1)$ ,  $c = 7.4046(1)$  Å,  $\gamma = 120^\circ$ . Cell vol = 639.06(1) Å<sup>3</sup>  
<sup>b</sup> $R_{\text{wp}} = 2.08\%$ ,  $R_{\text{p}} = 3.37\%$ ,  $\chi^2 = 1.9$

**Table 3** Selected bond distances for La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub>

| Bond       | Bond distance (Å)       |
|------------|-------------------------|
| La1/Ba1–O1 | 2.549(8) [ $\times 3$ ] |
| La1/Ba1–O2 | 2.562(8) [ $\times 3$ ] |
| La1/Ba1–O3 | 3.000(7) [ $\times 3$ ] |
| La2/Ba2–O1 | 2.508(9) [ $\times 3$ ] |
| La2/Ba2–O2 | 2.650(9) [ $\times 3$ ] |
| La2/Ba2–O4 | 2.900(7) [ $\times 3$ ] |
| La3–O1     | 2.793(3)                |
| La3–O2     | 2.546(2)                |
| La3–O3     | 2.646(6), 2.500(6)      |
| La3–O4     | 2.628(7), 2.500(7)      |
| La3–O5     | 2.353(1)                |
| Ge–O1      | 1.730(2)                |
| Ge–O2      | 1.748(2)                |
| Ge–O3      | 1.710(4)                |
| Ge–O4      | 1.778(6)                |

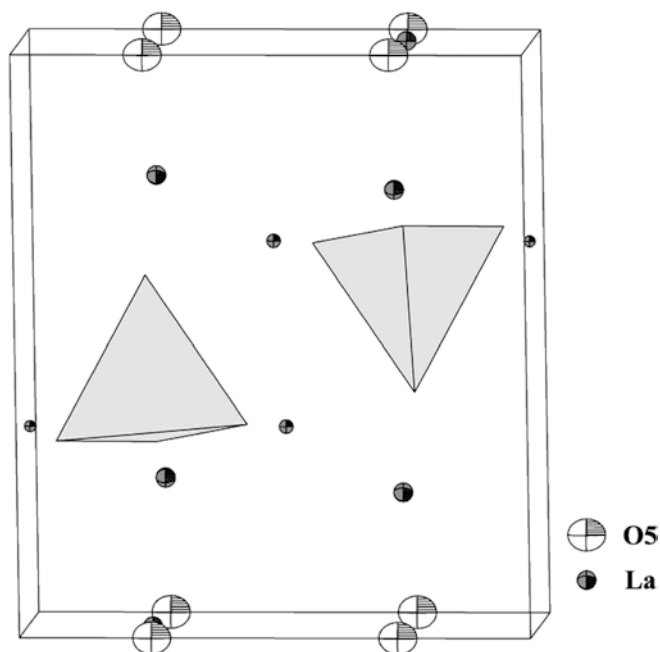
isotropic. This can also be clearly visually seen in Fig. 4, which shows the structure of La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub> including the anisotropic thermal ellipsoids for the channel oxygen atoms.

**Fig. 3** Observed, calculated and difference neutron powder diffraction profiles for La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub>

It is also noticeable that the channel oxygen position is very close to the ideal (0,0,0.25) position, consistent with a lack of disorder in the oxide ion channels in this sample. The lower anisotropy and lack of evidence for any oxide ion disorder within the channels is therefore consistent with the low oxide ion conductivity observed in this sample. As stated earlier, the low activation energies for oxide ion conduction from the impedance measurements for La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub> may be related to a small degree of non-stoichiometry introduced on sintering, as a result of some Ge volatility.

A final point to note from the refinement is the high thermal displacement parameters for the GeO<sub>4</sub> oxygen atoms (O1–O4). Previous refinements on silicate phases have shown similar results, and modelling studies have predicted that significant relaxation of the tetrahedra away from the channels is possible in these phases [5, 13, 14, 15, 16].

Neutron diffraction structural studies on the oxygen excess sample La<sub>9</sub>BaGe<sub>6</sub>O<sub>26.5</sub> will be performed shortly to compare with the data for La<sub>8</sub>Ba<sub>2</sub>Ge<sub>6</sub>O<sub>26</sub>. In particular, studies of the evolution of the structure with tem-



**Fig. 4** The structure of  $\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$  showing the anisotropic thermal ellipsoids for the channel oxygen (O5) atoms (tetrahedra =  $\text{GeO}_4$ )

perature are planned to try to account for the change in activation energy at high temperature.

#### Extended sintering studies on $\text{La}_{8.67}\text{BaGe}_6\text{O}_{26}$ and $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$

In order to examine whether Ge volatility was still a problem in the doped phases, two Ba-doped samples were subjected to extended sintering studies under similar conditions as previously studied for undoped  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  [10]. Both  $\text{La}_{8.67}\text{BaGe}_6\text{O}_{26}$  and  $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$  were heated for 5 days at 1500 °C. The two samples showed a significant mass loss (> 2%), with the X-ray pattern showing the appearance of  $\text{La}_2\text{GeO}_5$  as an impurity phase, which is consistent with Ge loss. The mass loss and changes in X-ray patterns observed were not as severe as for undoped  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  under similar conditions, but they would represent a significant problem in the use of these materials in a SOFC. In support of this, the conductivities of the samples showed a large decrease (by nearly three orders of magnitude) after the extended sintering treatment. The results

therefore show that although divalent cation doping helps stabilize the hexagonal apatite lattice to high temperature, the problem of Ge volatility in these phases is not overcome. This Ge volatility represents a serious problem, since even short-term sintering would be likely to result in loss of Ge from the surface of the electrolyte. This could then result in interfacial problems with the electrodes, due to the formation of thin insulating  $\text{La}_2\text{GeO}_5$  layers.

#### Bi doping

Bi doping was attempted to lower both the synthesis and sintering temperature. This was shown to be successful, although attempts to dope Bi into  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  according to the scheme  $\text{La}_{9.33-x}\text{Bi}_x\text{Ge}_6\text{O}_{26}$  ( $x = 1, 2, 3$ ) resulted in small impurities. In order to prepare single phase samples, co-doping on either the La or Ge site was found to be required. This co-doping has the effect of reducing the number of cation vacancies present in the sample, which may be the key feature in achieving single phase Bi-doped samples. A range of Bi-doped samples has been successfully prepared and these are presently under study. These phases are interesting not only for their oxide ion conductivity, but also for the fact that very few Bi-containing apatite phases have been reported in the literature.

Cell parameters and conductivity data for selected samples are given in Table 4. As shown for other systems, the lowest conductivities were observed for samples nominally stoichiometric on both cation and anion sites, with the highest conductivities observed for samples containing oxygen excess.

These preliminary studies on Bi doping have shown that it gives high-quality samples, with much lower sintering temperatures (1050–1100 °C) required. The lower synthesis and sintering temperatures should help limit Ge loss in such samples, although Bi volatility could be a problem instead. In addition, the presence of Bi means that the samples are not stable under reducing conditions at high temperatures. In confirmation of this, heating samples in  $\text{H}_2/\text{Ar}$  (5%/95%) at 900 °C for 12 h was shown to result in partial decomposition.

#### Conclusions

The Ge-based apatite phase  $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$  suffers from Ge loss and irreversible structural changes on sintering

**Table 4** Cell parameter (hexagonal cell) and conductivity data for selected Bi-doped samples

| Sample composition  | $a = b$ (Å) | $c$ (Å)  | $\sigma$ ( $\text{S cm}^{-1}$ ) (800 °C) | $E_a$ (eV) |
|---|-------------|----------|--|------------|
| $\text{La}_6\text{Bi}_2\text{Ba}_2\text{Ge}_6\text{O}_{26}$ | 10.024(4)   | 7.399(4) | 0.001                                    | 1.08       |
| $\text{La}_6\text{Bi}_2\text{Sr}_2\text{Ge}_6\text{O}_{26}$ | 9.911(3)    | 7.310(2) | 0.003                                    | 1.12       |
| $\text{La}_8\text{Bi}_2\text{Ge}_5\text{GaO}_{26.5}$        | 9.906(3)    | 7.335(3) | 0.02                                     | 1.10       |
| $\text{La}_{7.67}\text{Bi}_2\text{Ge}_5\text{GaO}_{26}$     | 9.903(1)    | 7.333(1) | 0.01                                     | 1.09       |

at high temperatures. Divalent cation substitutions (e.g. Ba) on the La site helps to stabilize the hexagonal apatite lattice to high temperatures, although problems due to Ge volatility at these temperatures remain. Bi doping lowers both the synthesis and sintering temperature, although such samples are not stable at high temperatures in reducing conditions.

The doping studies confirmed the importance of cation vacancies and/or oxygen excess for obtaining high oxide ion conductivity in these Ge-based apatite systems, similar to previously observed for the Si based systems.

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